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REVIEW

Durable water and oil repellents along with green chemistries: an overview

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Abstract

The phase-out of long-chain C8-based perfluorochemicals necessitates the textile industry to find the best alternatives to these durable oil- and water-repellent chemistries. Finding out the alternatives has resulted in a textile market where both fluorine-based and fluorine-free durable water repellent (DWRs) are available. These DWR substitutes depending upon their chemistries are categorized into four major groups: long-chain fluorinated polymers, hydrocarbons including the long-chain fatty acids, silicones, and inorganic nanoparticles. This paper discusses various DWRs regarding their structure, properties, performance, loss, and degradation processes and their effect on the habitat and human health. The alternative DWRs lack performance compared to fluorinated finishes and, most importantly, oil repellence. Degradation products from all DWRs alternatives diffuse to the environment. Research shows that hydrocarbon-based DWRs are the most environment friendly (including long-chain fatty acids), followed by silicone-based DWRs and fluorinated polymer-based DWR finishes. Industrial commitments will play an important role in reducing impurities from available DWR chemistries. Before approaching environment-friendly alternatives of required performance, it is better to select DWR finishes on a specific requirement and always counter the benefits of enhanced performance against the potential threats to the ecology and human beings.

Keywords Water- and oil-repellent finish · Fluorocarbons · Green chemistries · Environment friendly

Introduction

Nature is the key commander to human beings in inventing different technologies. The development in science and technology is remarkable with the onset of the twenty-first century. However, they have come with a price of increased global warming that led to sudden changes in climate. To sustain and be effective in a certain environment, we need appropriate apparel for working in such a harsh environment. As humans constantly search for excellence, the traditional textile paradigm shifted to multipurpose and functional textiles. Oil and water-repellent fabrics are engineered to save the wearer from outdoor weather conditions. The demand for modern functional textiles has increased daily, leading to the need for new technologies and materials (Saratale et al. 2020; Fahmy et al. 2017).

Cotton fabric is soft, comfortable, easy to handle, inexpensive, and biodegradable (Gao et al. 2016; Pan et al. 2019; Biltekin and Ayça 2019). Due to these specular properties, it has become the most promising and widely used material in the textile and cosmetic industry (Berendjchi et al. 2011; Bhuiyan et al. 2017; Mohsin et al. 2016a). However, it lacks oil and water repellency is one of the biggest drawbacks limiting its usage (Rabia et al. 2020). To make cotton fabric oil and water repellent, efforts have been continued by modifying cotton fabric chemically from the 1980s (Singh and Singh 2017; Han and Min 2020). However, these modifications should meet the criterion of green chemistry

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without disturbing its remarkable performance (Ferrero et al. 2017). Oil and water repellency (Xiong et al. 2012; Onar et al. 2015; Sharif et al. 2022a), ultraviolet protection (Stan et al. 2019), flame retardancy (Faheem et al. 2019) (Yang and Chen 2019; Bentis et al. 2020), antibacterial properties, self-cleaning (Chauhan et al. 2019; Vasileva-Tonkova et al. 2019), and wrinkle resistance are the other major functional properties desired for cotton fabric. These pivotal functional properties prodigiously increase their utilization in rainwear, sportswear, industrial end-products, medical equipment, and household applications (Schellenberger et al. 2019; Suryaprabha and Sethuraman 2017). Hydrophobic and oleophobic fabric can be obtained by applying paraffin repellents (Bashari and A. H. Salehi K, and N. Salamatipour 2020), silicone-based repellents (Khattab et al. 2020), acrylate backbone repellents, stearic acid–melamine repellents and fluorocarbon-based repellents, mainly C4-, C6-, and C8-based chemistries (Fahmy et al. 2017). A huge variety of traditional oil and water-repellent finishes are available in the market, as shown in Fig. 1. However, most are costly, toxic, hazardous to the environment, non-durable, or inefficient. The most promising, durable, and performance-efficient oil and water repellent are C8-based perfluorinated compounds. However, their use is under immense pressure as PFC's (perfluorocarbons) compounds release PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonic acid) on degradation. They are toxic and carcinogenic for humans and the environment (Zhao et al. 2012, 2016; Gargoubi et al. 2020). This review paper will provide a road map for the industry and the researchers to find possible ways forward.

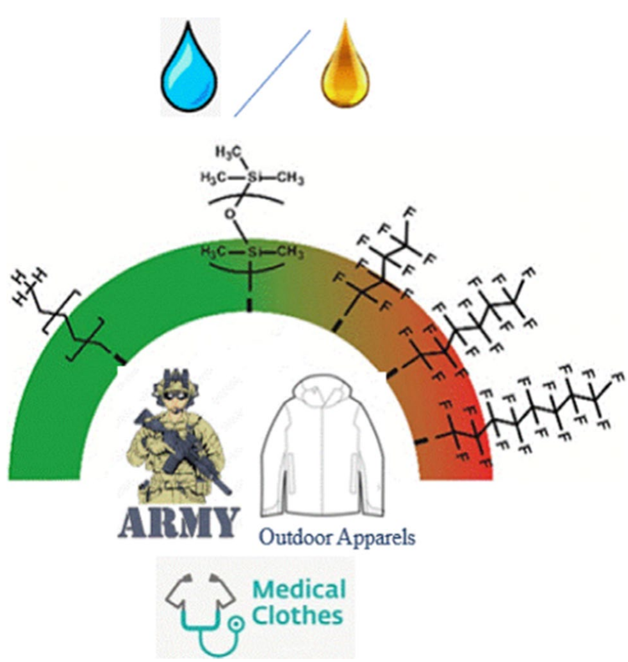

Fig. 1 Applications of oil and water repellent in functional textiles

Market share of repellent finishes

Among all chemicals produced worldwide, the share of the textile sector is almost 25% (Muthu 2015). The textile industry requires about 40% of the total chemicals as a finishing agents for clothing and apparel, as shown in Fig. 2. The size and global market share of textile finishing agents were around USD 9.2 billion in 2021 and are expected to get value to around USD 12.4 billion by 2026. Furthermore, it is envisioned to increase with a CAGR (compound annual growth rate) of 7.5% from 2021–2026. Figure 3 (MMR 2021) depicts the global market share of repellent finishes in 2021. Moreover, the usage of repellent finishes in Asia was the topmost, with a market share of 50%, as calculated in 2018.

With the increased usage of textile goods and chemicals worldwide, manufacturers and industries have come under severe scrutiny as they have adverse and hazardous effects on the environment and ecology (Senthil Kumar and Gunasundari 2018). Durable water and oil repellents (DWRs) are popular finishes coated onto the fabric to protect it from the soil, water, and oil. They also increase the life of the fabric. DWR finishes are mainly fluorinated C8-based polymers that exhibit water repellency and excellent oil repellency (Schellenberger et al. 2018; Liu et al. 2019). However, they degrade into long-chain PFOA and PFOS, which were brought to major concerns due to their adverse and toxic effects on the environment and human beings (Atav and Bariş 2016; Veen et al. 2016; Ma et al. 2018). Numerous efforts were made to eliminate these fluorine-based compounds (Onar and Mete 2016). Hence, many countries banned using these long-chain C8 fluorocarbons (Zhou et al. 2011).

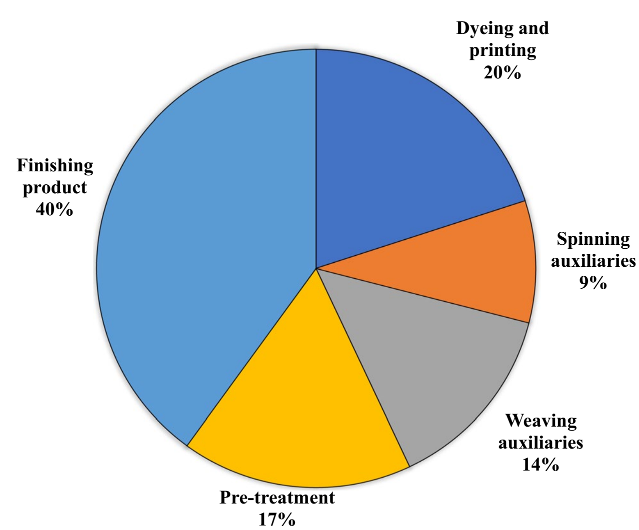

Fig. 2 Market share of auxiliary textile distribution

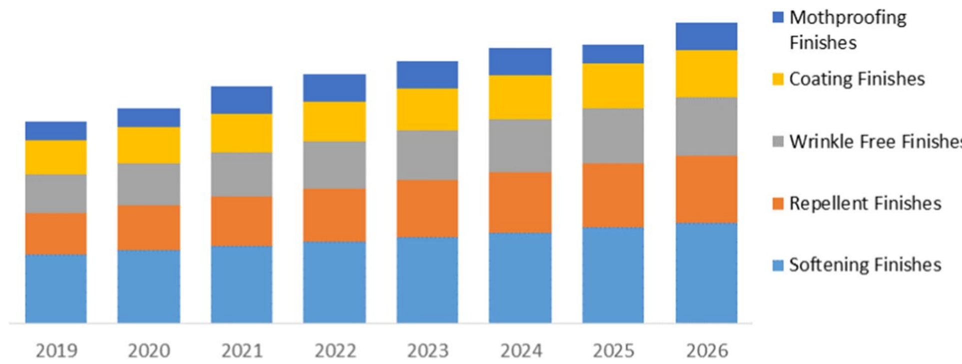

Fig. 3 Global functional textile finishing chemical market share till 2026 (MMR report; ID: 90605)

In 2011, a commitment was made by Zero Discharge of Hazardous Chemicals (ZDHC) group member brands to eliminate fluorinated DWR until 2020. Moreover, ZDHC enlisted fluorinated chemicals in the 11 priority chemicals list banned in process industries and international textile goods (ZDHC 2022). ZDHC also approached chemical manufacturers, industries, and regulatory agencies to find efficient, durable, and environment-friendly alternative short-chain fluorocarbons and fluorine-free DWR technology. As society's needs and demand for satisfaction rise higher every day, the functional performance of finishes is not the only interest nowadays.

People are also concerned about environmental and health issues along with outstanding and durable easy-care properties of the finishes. Thus, future textile industry trends are developing green products that do not harm human beings or the environment. In this pathway, famous worldwide brands started working to make their product 'green,' such as Levi Strauss & Co. was using PFCs to make their products water-resistant. However, from January 2016 onward, they eliminated the use of PFCs from their products and achieved water repellency as they started working on a safer alternative for humans and the environment. Another famous American brand, Zara, eliminated zero discharge of hazardous chemicals from its production chain in 2020 and moved toward product sustainability before the end of 2025. Moreover, Adidas also discontinued the usage of PFCs in their outdoor product in December 2017. Other well-known brands such as H&M, Nike, and Patagonia have provided PFC's free end-user products since 2020 (Patra and Pariti 2022).

Research now focuses on short-chain C4-based fluorocarbons free from PFOA and PFOS. They are a comparatively safer alternative to conventional C6- and C8-based fluorocarbons (Atav 2018; Mehta 2018). However, these short-chain fluoropolymers are less performance efficient, do not degrade easily, and are still hazardous for humans and the environment (Shabbir 2019). So, the requirement is fluorine-free chemistries to figure out the concerns. Some non-fluorinated water repellents are aluminum and zirconium compounds (Abidi 2018), paraffin waxes (Abo-Shosha et al. 2008), silicon repellents (Kasapgil et al. 2019), and polyurethane-based repellents (Bhuiyan et al. 2019). However, either they are toxic, non-durable, or less efficient. The long alkyl chain is a possible alternative to fluorocarbons (Liu et al. 2019). Long-chain fatty acids such as stearic acid (Zhang et al. 2019) and palmitic acid (Lee et al. 2014; Sharif et al. 2022b) are bio-based. They can impart water repellency by modifying the surface of cotton fabric, but their effects are much lower than fluorocarbons.

Mechanism of oil and water repellency

When a liquid droplet spreads on the textile substrate, the wetting phenomenon occurs due to the intermolecular interactions between the fabric surface and the liquid droplet. The various finishes with low surface energy or surface tension increase the oil and water repellency (Zhao et al. 2020; Ren and Zhao 2010). These finish coatings prevent the spreading of liquid droplets on the fabric surface (Zisman 1964; Schindler and Hauser 2004; Jung et al. 2020). The critical surface tension of the fabric surface should be less than the surface tension of the oil or water to repel them. The surface tension of water is 72 mN/m (millinewtons per meter) at 20 ℃, whereas the surface tension of oil ranges between 15 and 30 mN/m. Therefore, repellent finishes should lower the surface tension of treated cotton fabric below these limits for respective oil and water repellency. The long-chain hydrocarbon-based repellent coatings lower the surface energy of the treated cotton fabric to around 50 mN/m. Therefore, they can impart only appreciable water repellency with zero oil repellency. Fluorochemical finishes lower the surface energy of the coated fabric to below 30 mN/m and can exhibit sufficient oil and water repellency (Kissa 2001; Rastogi et al. 2013; Dekanić et al. 2018). Various application methods apply oil and water-repellent coatings onto the fabric, such as mechanical applications, chemical reactions, and coating films. Water- and oil-repellent finishes decrease the wettability of the fabric surface. Wettability can be obtained by evaluating the contact angle between a liquid droplet and a fabric surface at their interface. A contact angle of > 90°

shows that the substrate is hydrophobic, and a contact angle of < 90° shows that the substrate is hydrophilic, as shown in Fig. 4.

Water-repellent finishes

Various textile commodities like raincoats, bags, kitchen covers, and athletic wears require a water-repellent finish to make them easy to wear and durable. This can be achieved by using durable water-repellent (DWR) finishes. Among DWR, the most remarkable are fluorocarbon finishes. DWR finishes are long-chain perfluorinated chemistries having oil-, water-, and soil-repellent characteristics. These include chemicals plasma, perfluorooctanoic acid (C8), perfluorohexanoic acid (C6), fatty acids, dendrimers, silicone, paraffin waxes, and nanomaterials. The DWR finishes from textiles coated with DWR finishes diffuse to the water through leaching, wear, and tear and during the laundry and drying process. DWR chemicals also diffuse into the air through evaporation (Holmquist et al. 2016). The loss mechanism during the use of fabric is represented in Fig. 5. Some water- and oil-repellent finishes are given in Table 1.

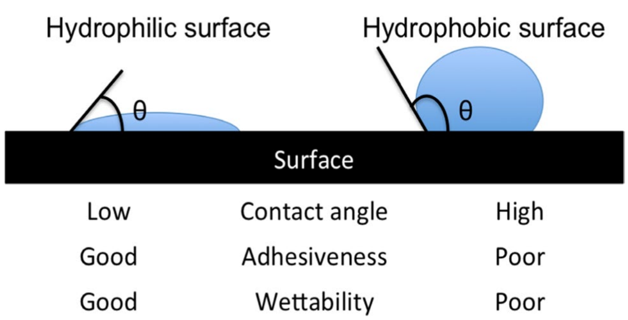

Fig. 4 The connection between wettability and contact angle (Gomes et al. 2013)

Nanotechnology approaches in finishing methods

The nanotechnology finishing methods can be a good method to improve the oil and water repellency and many other characteristics of cotton fabrics through various nanomaterials (Soane et al. 2003). Silanol-based ZnO nanoparticles were applied on cellulose activated via copolymerization of glycidyl methacrylate and acrylic acid (Mohamed et al. 2014; Shabbir and Mohammad 2017). The drop test resulted in greater than 30 min, thus inducing super-hydrophobicity to the cotton fabric. Ghasemi et al. (2018) prepared the superhydrophobic and antimicrobial cotton fabric by combining ZnO nanoparticles and octadecanethiol. The presence of a newly developed finish was confirmed by SEM analysis. Hydrophobicity imparted by the applied finish onto the cotton fabric was measured by the contact angle greater than 161°. Furthermore, the reduced surface energy of the fabric was also responsible for the reduction in bacterial attacks.

Fig. 5 Release of DWR chemicals during a usage phase of the garment (Holmquist et al. 2016)

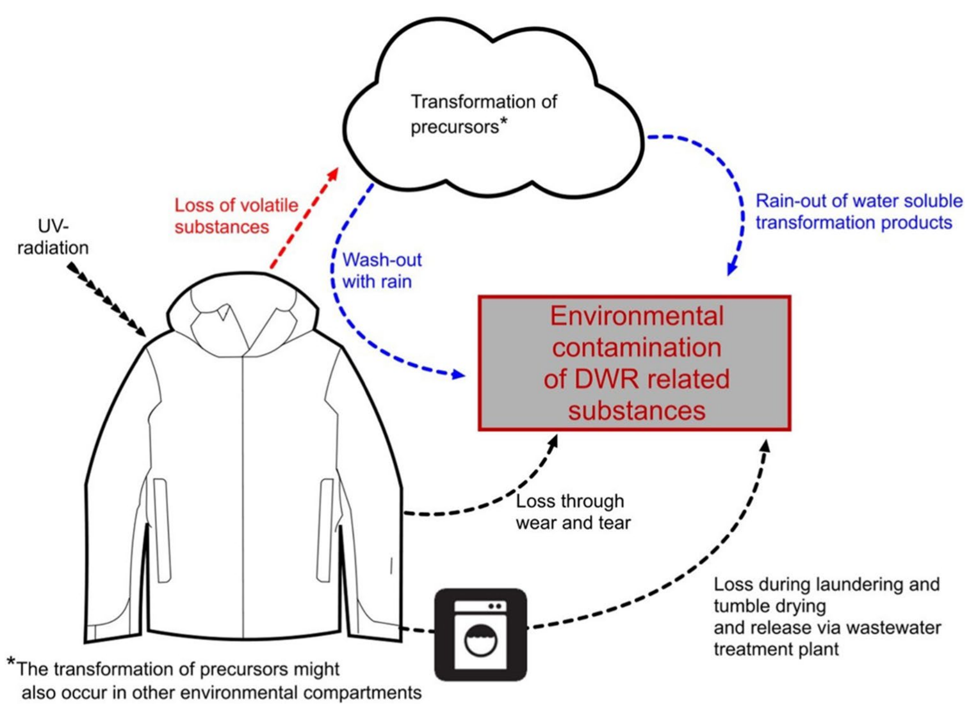

Table 1 Water- and oil-repellent finishes

Name of finishes	Summary
Metal salt finishes	Aluminum- and zirconium-based hydrocarbon compounds are water repellents (Emam 2019; Lewin 1984)
Paraffin repellents finishes	Hydrocarbons, paraffin wax, impart good water repellency but zero oil repellency (Islam and Asaduzzaman 2019)
	Paraffin wax or its blends with beeswax, vaseline, and carnauba wax can be used as water repellents (Fahmy et al. 2016; Kim et al. 2017)
	Applied to the fabric in many ways, such as dissolving the wax in an organic solvent, spraying melted wax on the fabric, padding the aqueous wax emulsion on the cotton fabric (Abo-Shosha et al. 2008; Choudhury 2017), and applying wax through layer-by-layer technique (Bashari and A. H. Salehi K, and N. Salamatipour 2020)
Glue and Gelatine-based finishes	Glue and gelatine combined with an aluminum salt increases the water repellency (Mohsin et al. 2016a)
Pyridinium-based finishes	Long-chain fatty acid derivatives such as stearic acid is attached to the pyridinium ring (Lu et al. 2019; Edward and Goswami 2018; Boukhriss et al. 2016)
Organo-metallic complexes	Aluminum and chromium-based organo-complexes can impart semi-durable water repellency to cotton fabric (Muresan et al. 2013). The most popular complex has been reported as Quilon, formed by combining chromium with stearic acid with high water repellency (Kissa 2018)
N-Methylol derivatives	The N-methylol compounds react with carboxylic acids, alcohols, and amines. These alkyl methylol compounds (e.g., stearamide-formaldehyde, stearyl-urea formaldehyde, and stearamide-melamine) form ether linkage with cellulose to impart durable water and wrinkle resistance (Schindler and Hauser 2004). These finishes have various issues, such as loss in tensile strength, fabric shade changes, and formaldehyde release (Rovira and Domingo 2019)
Silicone-based water repellents	Many silicone-based water repellents for cotton fabric, such as methyl hydrogen polysiloxane, dimethyl polysiloxane, polydimethylsiloxane (Moiz et al. 2016; Liu et al. 2018; De et al. 2005), and silica nanoparticles (Jeong and Kang 2017). New formulations such as CPS1000/TDI and CPS5000/TDI upon reacting monocarbinol terminated polydimethylsiloxanes (CPS) with 2,4-Toluene diisocyanate (TDI) at 100˚C for 90 min (Fahmy and Hassabo 2022)

Multifunctional cotton fabric such as hydrophobic, photochromic, crease-resistant, oleophobic antibacterial, and ultraviolet protection was made by coating it with a mixture of silica nanoparticles and spirooxazine followed by alkylsilane compounds. The homogenous coating application onto the cotton fabric was affirmed by scanning electron microscope and X-rays mapping (Ayazi-Yazdi et al. 2017). The finished cotton fabric depicted substantial hydrophobicity with a contact angle of 141°. The finished cotton fabric also indicates antimicrobial activity and ultraviolet blocking properties.

The cotton fabric was cationized using diallyl dimethyl ammonium chloride (DADMAC). Then, the cationized cotton fabric was treated with an aqueous solution of BTCA (butanetetracarboxylic acid), SHP (sodium hypophosphite), 0.5% TiO_2, and 0.5% of SiO_2. The fabric was then finished with stearic acid to further reduce the surface tension of the cotton fabric. Later, the treated fabric was assessed for hydrophobicity, air permeability, tensile strength, UV protection, and antibacterial activity, while SEM and XRD (Soane et al. 2003) characterized coated fabric.

Despite having the potential for oil and water repellency, nanotechnology is under scrutiny as it can pose risks to ecology, human safety, and health (Almeida and Ramos 2017). Moreover, nanomaterials are costly, can threaten mammals, and trigger breathing issues (Siegfried and Som 2007), as shown in Fig. 6. The above-mentioned issues restricted the use of nanotechnology in oil and water repellency (Jia et al. 2017).

Fluorocarbons finishes

The fluorocarbon finishes started in 1960 and became the most popular in the last decade of the twentieth century. The rise in consumer need for multifunctional textiles (e.g., water-, oil-, and soil-repellent textiles) stimulated the growth of fluorocarbon finishes (Moilliet 1963; Audenaert et al. 1999). These finishes provide outstanding oil, water, and soil repellency (Liu et al. 2019). A surface energy lower than 18 mN/m can be achieved by applying these finishes (Ma et al. 2018). The unique characteristics of fluorocarbons make them suitable for various applications (Sharif et al. 2022b; Almeida and Ramos 2017; Siegfried and Som 2007) and the most effective oil and water-repellent finish for textiles (Luo et al. 2020; Mazrouei-Sebdani and Khoddami 2011; Türk et al. 2015). In 1953, fluorocarbons as oil and water repellent, namely Scotchgard, had invented accidentally when few drops of fluorocarbon spill over Joan Mullin a 3 M Technician's tennis shoes (Audenaert et al. 1999). Till now Scotchgard is one of the best oil and water repellent.

An 8–10 perfluorinated carbon chain and CF3 as a terminal group are enough to achieve good oil and water repellency (Schindler and Hauser 2004). Uniform distribution of

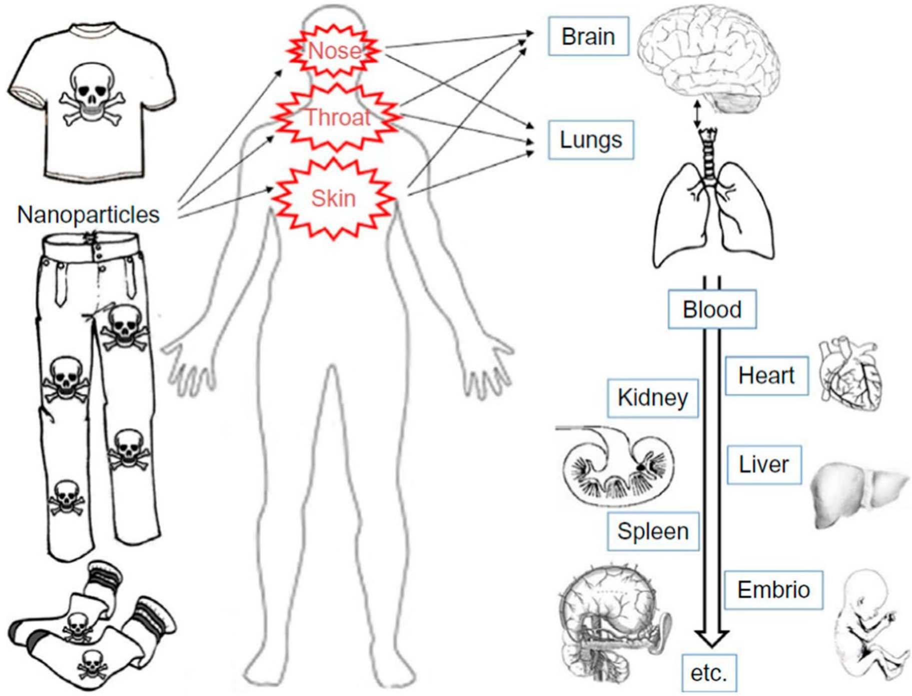

Fig. 6 Effects of nanomaterials on the human body (Saleem and Zaidi 2020)

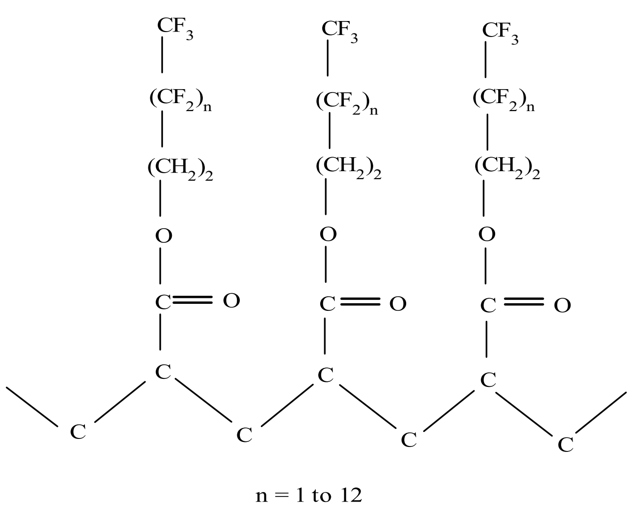

Fig. 7 Acrylic backbone of perfluorinated compounds (Mohsin et al. 2016b)

repellent, appropriate orientation, chemical structure, chain length of fluorocarbon, amount of applied finish, origin, and geometry of cotton fabric will determine the repellency rating of fluorocarbon finishes. Generally, perfluorinated acrylate having an acrylic backbone is an effective and durable oil and water repellent, as shown in Fig. 7 (Mohsin et al. 2013). There are several commercially available fluorocarbon products in the market, namely Scotchgard, Teflon, Nuva, and Asahigaurd by the companies 3 M, Teflon, Clariant, and Asahi, respectively.

Highly fluorinated finishes provide a higher water and oil-repellency rating (Ferrero and Periolatto 2013). A group of researchers achieved outstanding water repellency with a water contact angle greater than 150° by using fluorinated polymers on cotton fabrics. The well-known fluorinated water and oil-repelling agents are fluorocarbon finishes that reduce the cotton fabrics' surface energy (Shi et al. 2013). However, the long-chain perfluorocarbon having carbons atoms greater than seven, such as perfluorooctanoic acid, has serious health related issues (Zhao et al. 2012, 2016; Ye et al. 2013). Hence, these long-chain finishes (e.g., C8 fluorocarbons) are restricted in many countries due to customer awareness and pressure from several social organizations (Zhou et al. 2011).

PFCs are mostly applied onto the fabric by the pad-dry-cure method. Curing treatments are responsible for the orientation of the fluorocarbon chain onto the fabric, which is most important in attaining optimum repellency. Washing of fabric changes the orientation of fluorocarbons applied onto the cotton fabric, but re-orientation can be achieved after ironing. Furthermore, there are finishes available in the market that can be re-oriented in air drying.

The performance of fluorocarbon finishes reduced remarkably after successive washing. However, washing durability can be increased by adding cross-linkers to the recipe (Mohsin et al. 2013). N-methylol agents were used as an effective and economical cross-linker for fluorocarbon finishes. Despite this, they release formaldehyde which limits their use (Yang and Chen 2019). Therefore, several formaldehyde-free cross-linkers are part of past and current research. Polycarboxylic acids are the most promising and potential replacement for formaldehyde-based cross-linkers (Xiao et al. 2018).

Environmental aspects of fluorocarbon finishes

The literature has reported that fluorocarbons based on C8 chemistry are excellent textile finishes to impart exceptional oil and water repellency. However, these finishes harm humans and the environment (Sunderland et al. 2019; Mazzon et al. 2019). They are carcinogenic and toxic to the reproduction system (Lei et al. 2017) and cause many other diseases, such as immune toxicity, chronic kidney disease, liver tumor, and behavioral disorders (Jian et al. 2017). Therefore, C8 chemistry and its harbingers have been withdrawn completely from the textile industry since 2015. Moreover, C8- and C6-based fluorocarbons are part of 11 priority chemicals that ZDHC banned in the textile industry (ZDHC). Accordingly, scientists and commercial manufacturers are interested in finding non-bio-accumulative environment- and human-friendly short-chain fluorocarbons.

Existing substitutes to C8-based fluorocarbons are less hazardous short-chain C6-based fluorocarbons (Atav and Bariş 2016). However, they lack in durability and oil and water repellency. Also, the research is now focusing on developing C2 or C4-based oil and water-repellent finishes for the textiles. A company, "3 M, has developed new C4-based fluorocarbons". Even though the short-chain alternatives seem to replace the long-chain repellents effectively, they are less efficient than long-chain perfluorinated finishes (Gargoubi et al. 2020). Though the short-chain fluorocarbons (e.g., C6 or C4 fluorocarbon) are less dangerous to the ecology, the reduction in the carbon chain made them less effective (Atav 2018; Mehta 2018). This short-chain fluorocarbon finishes exhibit poor performance and durability.

Moreover, they are persistent, do not degrade easily, and remain a potential threat to humans and the ecology (Mehta 2018; Shabbir 2019). So novel research is on the roadmap to find the best alternative for these fluorinated chemistries that should be fluorine-free, eco, and human-friendly finishes as oil and water repellents for textiles. So, researchers are endeavoring to prepare hydrophobic and oleophobic cotton surfaces with multifunction properties.

Fatty acids—stearic acid and the palmitic acid

Fatty acids such as stearic and palmitic acid could be used as an alternatives to fluorinated finishes (Suryaprabha and Sethuraman 2017; Xue et al. 2010; Zahid et al. 2017; Cai et al. 2018). The fatty acid undergoes an esterification reaction with cellulose without degradation (Vaca-Garcia et al. 1998; Yidong and N. A. N., 2016). Stearic acid and palmitic acid can improve the water repellency of cotton fabric (Pan et al. 2019; Sharif et al. 2021; Patil and Netravali 2019; Bashiri Rezaie et al. 2019). These fatty acids are bio-based and can be used as water-repelling agents (Sharif et al. 2022a; Zhang et al. 2019; Lee et al. 2014). Stearic acid (octadecanoic acid) is a saturated fatty acid with eighteen carbon atoms. Its chemical formula is $C_{18}H_{36}O_2$ or $C_{17}H_{35}CO_2H$. Palmitic acid (hexadecanoic acid) is a saturated fatty acid with sixteen carbon atoms. Its chemical formula is $C_{16}H_{32}O_2$ or CH_3 $(CH_2)_{14}COOH$. The structure of both fatty acids is provided in Fig. 8. Fatty acids are derived easily from various origins, such as plants, animals, and dairy products (Agrawal et al. 2017). They are classified as safe (Caba et al. 2012). They are a favorable water repellent for cotton fabrics and other materials (Agrawal et al. 2017; Jiang et al. 2018).

Green products for water repellency on textiles

The concept of green chemistry is to produce green finishes and their manufacturing processes to decrease or eliminate lethal chemicals' usage and production, as shown in Table 2 (Anastas and Eghbali 2010). The outset of green chemistries started in the 1990s as countries like the USA, UK, and Italy (Tang et al. 2008) took the initiative of environment-friendly chemicals. The restriction was placed on the companies by the EU's REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) and the USA TSCA (Toxic Substances Control Act) to get permission from the legislative agencies before the manufacturing of any new and novel formulation, thus assuring only the essential chemistries introduced in society. Since November 2020, the European Union has outlawed the usage of thirty-three chemical compounds in the textiles industry, labeling them as mutagens, carcinogens, hazardous, and toxic for the reproductive system (Christie 2007).

According to the green chemistry theory, durable water repellent (DWR) should be free from toxic fluorocarbons. In this regard, the biomimicry principle is the basis of new developments in the design and production of finishes taken from nature's best biological entities and used to cope with ecological issues. The technological giants are on the roadmap to find sustainable water-repellent

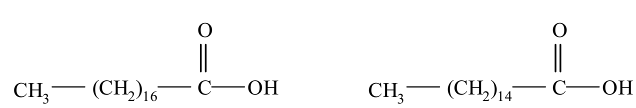

Fig. 8 Structures of **a** stearic acid and **b** palmitic acid

Table 2 Noxious effects of water- and oil-repellent finishes on human beings and ecology

Oil and water-repelling agents	Effects	Reference
Long-chain fluorochemicals	Carcinogenic, reproductive, and developmental disorders	Sharif et al. (2022a)
Short-chain fluorochemicals	Persistent and are less toxic to the environment	Shao et al. (2021)
Siloxanes, paraffin wax	Paraffin waxes are less permeable. Siloxanes are minor toxic but release harmful wastewater	Bashari et al. (2020)
N-Methylol derivatives	Less hazardous, however, stearic acid melamine resins release toxic and carcinogenic formaldehyde	Rovira and Domingo (2019)
Polyurethanes	The diisocyanate is a major part of polyurethane that can cause an allergic reaction to the lungs and skin. It also irritates the eyes, nose, throat, and lungs	Whittaker and Heine 2018)
Nanoparticles	They are toxic and accumulate in the kidney, spleen, liver, etc.	Saleem and Zaidi (2020)

chemistries. Zelan™ R3, based on renewable resources produced by Huntsman and Chemours, is a fluorocarbon-free and more durable water-repellent than existing non-fluorine finishes (Corporation, n.d.). Another fluorine-free water-repellent compound is Altopel™ F3, formulated by Bolger & O'Hearn Inc (Yip 2020). The polymer is also used to produce greener water-repellent garments. INSQIN®, developed by Covestro, is based on a waterborne polyurethane (PU). It is free from solvent and dimethylformamide toxin and only consumes almost 5% of water (Martin and Martin 2016). Rudolph group produced a novel oil and water-repellent finish called Bionic Finish Eco®, a dendrimers derivative (Failed 2019).

Contact angle greater than 150° is achieved by lycopodium and natural wax, plant-based filler materials, resulting in superhydrophobic finishes, as shown in Fig. 9. These coatings are mostly natural substances and do not include nanoparticles or other heat treatments (Morrissette et al. 2018). Another water-repellent finish is obtained by applying Carnauba wax to the fabric applied by a layer-by-layer technique. The wetting contact angles for cotton and nylon samples were 131.9° and 131.4° that reduced to 101.7° and 102.4° upon successive washings (Bashari and A. H. Salehi K, and N. Salamatipour 2020). Figure 9 represents the green chemistry used in formulations of water-repellent finishes.

Addition of cross-linkers in the water and oil repellents

The researchers added various substances in the C6 and C4 based fluorocarbons to increase repellency and durability. Modifying vegetable oils with trifluoroethanol and tetrafluoro propanol imparts appreciable water repellency (Khattab et al. 2020; Schellenberger et al. 2018), combining dendrimers with fluorocarbons to reduce their amount and acquire remarkable oil and water repellency.

In past, formaldehyde-based cross-linkers (e.g., dimethylol dihydroxy ethylene urea) were mostly used with fluorocarbons. For instance, N-methylol agents have been used as an effective and economical cross-linker for fluorocarbon finishes. However, they release formaldehyde which limits their use (Yang and Chen 2019). Among formaldehyde-based cross-linkers, DMDHEU (1, 3-dimethylol-4,5-dihydroxy ethylene urea) was the most attractive as it is an economical and efficient cross-linker (Haule et al. 2012;

Fig. 9 Green products in water-repellent finishes (Raj et al. 2022)

Chowdhury et al. 2018). However, formaldehyde can cause skin allergy, eye and respiratory tract irritation, headaches, and breathing issues. Moreover, it is toxic, a nuisance, and carcinogenic to humans (Mommer et al. 2020; Barbosa et al. 2019). Formaldehyde-based cross-linkers are one of the most effective cross-linkers. However, these substances are very lethal to humans. Certain cross-linkers (e.g., butanetetracarboxylic acid) are non-formaldehyde but are too expensive. Hence, formaldehyde-free and economical cross-linkers were employed with fluorinated repelling agents to enhance oil and water repellency (Mohsin et al. 2016a). There are many formaldehyde-free cross-linkers (Fig. 10). The most effective alternatives of formaldehyde-based cross-linkers are polycarboxylic acids (Xiao et al. 2018; Hashem et al. 2011; Dehabadi et al. 2013; Min and Choi 2018). Polycarboxylic acids with more carboxyl groups (e.g., 4–6 carboxyl groups) provide more efficient cross-linking.

The esterification reaction between polycarboxylic acids and cotton fabric can be accomplished in two steps. Firstly, the cyclic anhydride intermediate forms through the dehydration of two adjoining carboxylic acid groups (Dehabadi et al. 2012; Trask-Morrell and Andrews 1991; Lin et al. 2016). Then, this intermediate acid anhydride undergoes a reaction with a hydroxyl group of cellulose to form an ester, as shown in Fig. 11.

Citric acid is a carboxylic acid that is bio-based, less costly, easily available, and generally used cross-linker (Ahmed et al. 2021; Qutab et al. 2021; Taherkhani and Hasanzadeh 2018). The literature reported citric acid as an excellent finishing chemical for cotton fabrics (Mohsin and Sardar 2020). For instance, researchers (Mohsin et al. 2013) added citric acid to Genguard L-19296 (e.g., fluorocarbon-based acrylate polymer). It achieved a water repellency rate at 6 and an oil repellency rate at 1 even after 20 washes. In contrast, when Genguard was used alone, the water repellency was 3, and oil repellency was zero after only five washes. Hence, formaldehyde-free cross-linkers improved the oil and water repellency when used with fluorinated

Less hazardous synthesis	Design benign chemicals	Renewable feed stock
• BTCA • Citric acid (CA) • Itaconic acid (IA) • Carboxylic polyaldehyde sugar	• BTCA • Citric acid (CA) • Itaconic acid (IA) • Acrylol malic acid (AMA)	• Chitosan • Chitosan citrate • Sericin • Itaconic acid (IA) • Different vegatable oils

Fig. 10 Classification of cross-linkers

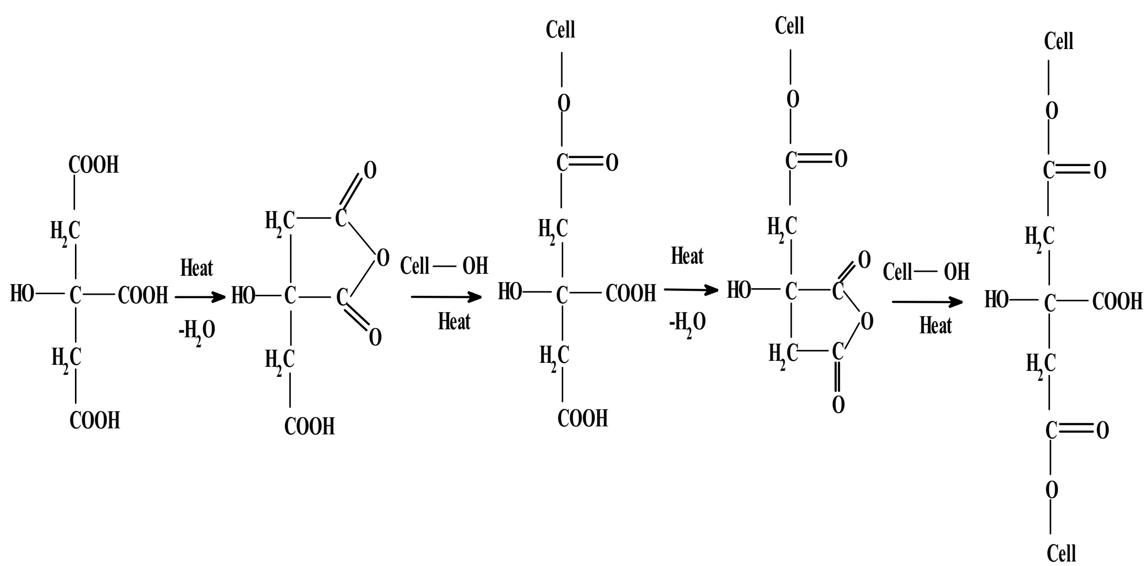

Fig. 11 Mechanism of the esterification reaction (Lam et al. 2011a, 2011b; Ji et al. 2016)

water and oil repellents. The performance of fluorocarbon finishes reduced remarkably after successive washing. In addition to citric acid, another carboxylic acid, maleic acid, has also been reported as a good cross-linking agent (Sharif et al. 2022a; Sarwar et al. 2019). The chemical structures of some carboxylic acids are shown in Fig. 12. For instance, it incorporated maleic acid in a commercial C6-based fluorocarbon repellent and attained excellent oil and water repellency and durability (Mohsin et al. 2016b). Other carboxylic acids include itaconic acid (Gupta et al. 2008; Yang et al. 2000), acrylic acid (Udomkichdecha et al. 2003), and succinic acid (Karimi et al. 2010; Afinjuomo et al. 2019).

Conclusions and recommendations

Many oil and water-repellent finishes are available in the market nowadays. This review paper categorizes them as fluorocarbon finishes, silicone-based water repellents, paraffin waxes, long-chain fatty acids, and nanoparticles. The most effective, unique, and durable repellents finish for textiles is perfluorinated polymer, as they can resist oil/stain, water, and soil. The silicone-based water repellents with PDMS backbone [–Si $(CH_3)_2O$–] exhibit high water repellency and softness in finished fabrics. Paraffin waxes are less air permeable and less durable to washing. The oleophobic and hydrophobic performance of non-fluorinated, biodegradables, and environment-friendly DWRs is comparable with C6- and C4-based fluoropolymers and slightly less than C8-based fluoropolymers. Long-chain fatty acids such as stearic and palmitic acids are bio-based and can be used as a hydrophobic finish. However, they lack durability; only repel water, and higher concentrations are needed for required repellency. Polymerization of long-chain fatty acids with polycarboxylic acids resulted in durable water- and oil-repellent finishes. Stain/soil repellency is not always a priority for outdoor apparel. However, non-fluorinated DWRs show little resistance to stains obtained from liquids with high to intermediate surface tension, whereas they have zero repellency from low surface tension liquids.

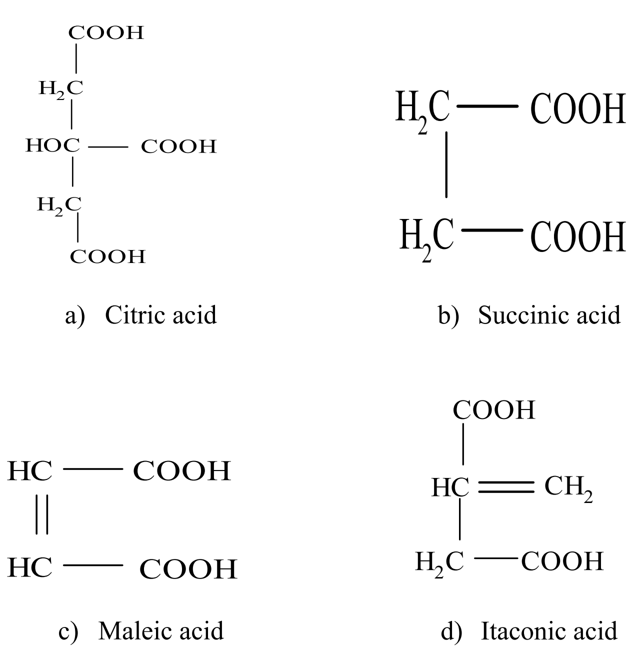

Fig. 12 Structure of **a** citric acid, **b** succinic acid, **c** maleic acid, and **d** itaconic acid

Developments in new DWR technologies are continued as the long-chain fluorinated polymers are being weeded out due to their environmental and health constraints. With the ambition to improve the ecology and human health, DWR finished textile products phased out fluorinated compounds completely in 2020 as they are persistent in the environment and hazardous. PFASs, highly non-biodegradable chemicals, when released into the environment, will result in nearly irreversible exposures on local (e.g., contaminated groundwater) and planetary scales. Short-chain fluorinated polymers based on hydrocarbons and silicones are improved compared to the C8-based long-chain fluoropolymers. However, these three groups of DWR substitutes are not completely concern-free. Although C6- and C4-based fluorocarbons are less persistent and bio-accumulative than C8 Fluorocarbons, they are still a threat if released into the environment. Silicone-based DWRs are also a red alert to human health, ecology, and fate endpoints. However, they are less nagging as compared to PFASs. Paraffin waxes are currently attaining market attention despite their possible hazards. Several studies confirmed that nanotechnologies have toxic effects on human health and the environment.

Sustainable practices are based on green chemistry. Principles of green chemistry will be adopted in the textile industry after knowledge of the life cycle of hazardous substances and the inefficiencies of the currently available manufacturing processes, usage, and disposal. So, green chemistry techniques are thus a win to win for the industry and society, improving cost-effectiveness and cooperation over compromise. Ethical trading, a net zero carbon footprint, zero-waste production, and healthier lifestyles are valuable benefits of adding green chemistries to the textile industry. DWRs should be further improved to achieve the required market need without disturbing nature and the environment. Based on the hazardous evaluation of DWRs, C8-based side chain perfluorinated polymer DWRs should be used only when oil/stain repellency is necessary. Otherwise, fluorine-free DWRs, particularly hydrocarbon DWRs, should be preferred for daily use where only hydrophobicity is required as they are less harmful to ecology. Silicone-based DWRs can be less lethal if residues of cyclic methyl siloxanes are further decreased. Till environmentally safe DWRs are available in the market, producers of hydrophobic garments should be careful in considering DWR, with the target to reduce the release of dangerous chemicals.

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Declarations

Conflict of interests The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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